GRAFT POLYMERIZATION. I. PRELIMINARY RESULTS WITH ACRYLATE ESTERS*

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ABSTRACT

The graft polymerization of ethyl and butyl acrylates onto chrome-tanned sheepskins was investigated and the conditions for reproducibly effecting the reaction have been established. For a number of reasons, butyl acrylate was found to be the monomer of choice. The product containing 13 percent poly(butyl acrylate), at least partially grafted to the collagen, had an increased thickness, the appearance of having been fatliquored, and a high degree of area stability. In addition, it had not suffered any decreases in shrinkage temperature or strength. The process was also applied to chrome-tanned kangaroo skins with the same beneficial results.

INTRODUCTION

Although leather is a versatile material and is still the preferred material for shoemaking, it lacks some desirable properties. In contrast to many synthetic substitutes, leather lacks uniformity and is subject to chemical deterioration, water penetration, and abrasion damage or scuffing. To overcome these deficiencies it is common practice to impregnate or coat leather with various preformed polymers. Unfortunately, these treatments are not permanent in that the polymers are only deposited in or on the leather and are not covalently attached. In some cases, some of the more desirable properties of the leather suffer as a result of these treatments. An alternative to this is the graft polymerization of various monomers directly onto the leather. The application of this process to cotton, starch, cellulose, and wool (1–5) has been investigated rather extensively over the past several years and appears to show much promise as a means of improving the properties of these natural products. It was to be expected that this same process could be applied to collagen, the major protein of animal hides and skins, and that such modified collagen might result in leathers with new and improved properties.

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Some preliminary work has been reported (6, 7) on the grafting of a few vinyl monomers onto hide powder and pickled buffalo hide and this latter has been converted into leather; however, little information is available on the properties of such products. Grafting of methyl methacrylate onto collagen has also been reported by Russian workers (8–11) but, again, the reports are lacking in detail. A rather extensive review article has recently appeared covering the graft polymerization of vinyl monomers onto proteins in general (12).

In this paper we are reporting our preliminary results on the application of the graft polymerization process to chrome-tanned sheepskins and kangaroo skins and the properties of the leather made from these. We recognize that a part of the polymer formed in these chrome-tanned skins may be homopolymer and not grafted polymer. The extent of this will be investigated in a later publication. However, the association of the homopolymer with the grafted polymer makes this a different product than would be obtained by simple deposition of the preformed homopolymer in the leather.

EXPERIMENTAL

Apparatus, Chemicals, and Skins

Ethyl and butyl acrylates were obtained from Rohm and Haas Company.† They contained 15 p.p.m. and five p.p.m. of the monomethyl ether of hydroquinone (MEHQ) as inhibitor, respectively. In some cases attempts were made to remove this from the ethyl acrylate; however, at these low levels, removal was not necessary. The ceric ammonium nitrate (CAN) was obtained from the G. Frederick Smith Company and the potassium persulfate ($K_2S_2O_8$) was Fisher Scientific Company certified grade. Commercial chrome-tanned Nigerian sheepskins were cut into eight-inch squares for use in the preliminary experiments studying the effects of variations in the treatment. Whole skins, as well as commercial chrome-tanned kangaroo skins, were used in the later studies.

The small-scale polymerization experiments on eight-inch square pieces were run on a tumbling machine in tightly sealed two-quart Mason jars. Full skins were treated in a large stainless-steel and glass-lined Meissner mill (approximately 24 inches inside diameter, 12 inches wide), revolving at a speed of ten r.p.m.

Graft Polymerization Procedure

Various procedures were investigated using the 8-inch squares of chrome-tanned Nigerian sheepskins to establish the effects of the different reagents and conditions. Some of these are briefly described in the Tables (I and II) and are discussed later. The procedure which was found to work best was adopted for whole skins and is outlined and described below. The percentages are based on the weight of the blue stock.

†Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

Blue Stock (after neutralization)	100%
Water	200%
Surfactant	
C_{20} alkene sulfonate	0.5%
Alkylphenoxy polyethoxy ethanol	0.5%
Monomer	up to 25%
Initiator	
Potassium persulfate	1%
Sodium bisulfite	0.3%

Flush with CO_2, seal, and run for up to 24 hours.

The water, surfactant mixture, and monomer were generally added to the mill first along with the CO_2. This latter could conveniently be added in the form of dry ice which, in contact with float, rapidly evaporated and filled the mill with CO_2. After these were all added and mixed, the initiator was added and dissolved, followed immediately by the addition of the skin. The mill was then sealed and started in motion. Some venting of CO_2 was sometimes necessary shortly after starting the mill in motion if all the dry ice had not evaporated; however, a slightly elevated pressure was beneficial. At the end of the run, both the pH of the spent liquor and the shrink temperature (T_s) of the treated skin were measured. Usually, the spent liquor was clear but a strong monomer odor persisted. The treated skin was washed in running tap water for several hours, wrung as dry as possible by hand, and then set out on the toggle rack to air-dry overnight. Aliquots (approximately five grams) of the air-dried treated skin were ground through a Wiley mill and stored in tightly sealed bottles for analysis. Moisture, ash, and total nitrogen were obtained on these samples.

Total N Determination

Approximately 50 mg. of the ground, treated hide sample was weighed out on the analytical balance for semimicro Kjeldahl nitrogen determination. These values were reported on a moisture- and ash-free basis. The moisture was determined by drying the samples to constant weight in the vacuum oven at 50°C. and the ash values were obtained by heating the samples at 600°C. for two hours.

Shrinkage Temperature (T_s)

T_s was measured by placing $^3/_{16}$" × 2-¼" specimens in specially designed holders in a water bath and observing the temperature at which contraction or shrinkage first occurred (13).

Tensile Strength

The tensile strength determinations were made according to the accepted procedure (14). The tests on all skins were made in triplicate and samples were taken from the butt area of the skin parallel to the backbone.

In addition to the tensile strength, thickness, elongation, and breaking load were also measured.

Permeability to Water Vapor

The water-vapor permeability method is given in the ALCA method E 32 (15). Samples were taken from the same areas of each skin near the backbone and the determinations were made in a constant temperature and humidity room with circulated air maintained at standard conditions (24°C. ± 1°C. and 50 ± 2 percent R.H.).

Perspiration Resistance

The perspiration resistance was determined by a standard method (16), with minor modifications as follows: (a) smaller test specimens meauring 2-¼″ × 2″ were used, (b) complete penetration of the perspiration solution was obtained by evacuating the immersed samples in a desiccator, and (c) a slightly modified artificial perspiration solution was employed.

Ball Burst

Again, a standard method was used (17) on the butt areas of the skins. All tests were made only once, but thickness, extension, and load were also measured.

Stitch Tear

The accepted ALCA method E 13 (18), using a double hole with the cut parallel to the backbone in the butt areas of the skins, was employed. Only one test was made per skin.

DISCUSSION AND RESULTS

In considering the optimum conditions for graft polymerization of various vinyl monomers onto hides and skins, a number of factors must be considered. These include the type of substrate or raw material, concentration and type of monomer, concentration and type of initiator, pH, and temperature and time of reaction.

Many types of collagen substrate in various stages of leathermaking, such as native pelt as well as limed, bated, pickled, and chrome-tanned skins, were considered for graft polymerization. All except the last of these are not stable forms of collagen and, from a practical viewpoint, the introduction of polymer into the collagen structure at any of these pretanning stages may interfere with the later wet processes. However, Rao and coworkers (6) have applied graft polymerization to pickled stock and have reportedly converted this treated material into leather. Even so, when all these things were taken into consideration, chrome-tanned stock still appeared to us to offer the best substrate. This material is already stabilized and is available at a convenient stage of the wet processing cycle.

It is at this stage that many tanners sort their stock and also, in the side upper leather industry, the stock is usually split at this stage and retanned if necessary. It was also felt that such treatment of chrome-tanned stock might eliminate some of the later finishing operations and would be expected to give a more uniform product. In fact, on the basis of our studies, graft polymerization of chrome-tanned skins with acrylates produced a material which, because of its flexibility, appeared to have been fatliquored.

A large number of monomers can be used in the graft polymerization procedure, including acrylates and methacrylates, acrylamides, vinyl chloride and vinyl esters, vinyl pyridine and pyrrolidone, styrene, acrylonitrile, and allyl esters, as well as others. Only a few have been investigated to date. Acrylates were used initially because of their ease of polymerization, commercial availability, and low price. The higher acrylates in general have a rather low toxicity but still must be used with some degree of caution. Some low molecular weight members of this family, such as methyl and ethyl acrylates, are lachrymators and, because of their high vapor pressures, are more toxic and flammable than the others. However, many of the monomers are used on a very large scale by the plastics industry and considerable information is available on these properties.

A number of materials can be used to initiate the graft polymerization process. Some of the more common are ceric salts, persulfates, and peroxides. From these we chose to use persulfates and ceric salts in our initial studies. The use of these is discussed in the previously mentioned review paper (12) and theories concerning the interactions of the persulfates with proteins have been proposed (19). Ceric salts as initiators of polymerization are effective at room temperature; however, persulfates and peroxides require elevated temperatures (up to about 80°C.). These oxidizing agents, such as persulfates, can be used in combination with reducing agents, such as bisulfites, to form reduction-oxidation (redox) systems which are capable of producing free radicals at room temperature and thus acting as low temperature initiators. In our experiments, the persulfate/bisulfite redox system carried out in the absence of air and at room temperature proved to be very effective. Ceric salts are reported (20) to take part in similar types of reduction-oxidation reactions themselves with the functional groups in proteins; however, these were not as effective as the persulfate/bisulfite systems.

The effect of the atmosphere used in the graft copolymerization method is an important consideration. While polymerizations carried out under nitrogen are satisfactory, a CO_2 atmosphere to exclude air can be simply and readily obtained by the addition of dry ice to the polymerization mixture.

The data in Table I show the effect of increasing amounts of initiator alone on the uptake of ethyl acrylate by chrome-tanned sheepskin. Increasing the amount of ceric ammonium nitrate (CAN) resulted in a dramatic increase in the polymer uptake to about 37 percent at the five percent level of initiator. The T_s, however, was adversely affected by levels of this initiator greater than one percent.

TABLE I

EFFECT OF INCREASING AMOUNTS OF INITIATORS ON THE UPTAKE OF ETHYL ACRYLATE (EA) BY CHROME-TANNED NIGERIAN SHEEPSKINS

Expt. No.	Treatment Given*	% Polymer in Product†	T_S (°C.)	
			Start	Finish
1	2% CAN	11.7	97	92
2	3% CAN	12.1	99	88
3	5% CAN	36.8	99	83
4	2% $K_2S_2O_8$	4.0	92	97
5	3% $K_2S_2O_8$	5.2	100	99
6	5% $K_2S_2O_8$	10.0	99	98

*Treatment on eight-inch squares using 200 percent water, 25 percent EA, one percent surfactant, the indicated amount of initiator, and an atmosphere of carbon dioxide. All percentages are based on the neutralized blue weight of the skin. CAN is ceric ammonium nitrate.

†Percent polymer calculated from nitrogen determination, using 17.43 percent as value for nitrogen content of control (no polymer).

The treatments with CAN were carried out at pH 1.5–2.0 and a considerable amount of oxidation of the chrome apparently occurred, resulting in a off-colored product. In addition, the sample treated with five percent initiator had shrunk approximately $^1/_3$ of its original dimension. On increasing the pH of this system to five by the inclusion of sodium acetate, polymer was deposited on the surface of the skin, which resulted in a very tacky product. With increasing amounts of persulfate, up to five percent, only a slight increase in the uptake of polymer was observed but, unlike the case of CAN, the T_s was not affected.

The data in Table II demonstrate the effectiveness of the persulfate/bisulfite system on the polymerization of ethyl acrylate in Cr-tanned Nigerian sheepskin. No polymer was taken up in the system where the reducing agent ($NaHSO_3$) was omitted. Even when the bisulfite was added in the presence of air, only a slight uptake of about five percent was observed. However, in the absence of air a product containing about 20 percent polymer and 80 percent dried chrome-tanned substrate, based on the nitrogen analyses, was obtained. The T_s values were not affected by this treatment. Thus, adequate conditions for this would appear to be those given in either Experiment No. 5 or No. 6. Although the surfactant appears to have little or no effect here, it would be expected to with butyl acrylate, which is less soluble in water than ethyl acrylate.

We next applied this treatment to full chrome-tanned sheepskins, using both ethyl acrylate and butyl acrylate. These two monomers polymerized readily in the substrates and we obtained products with as much as 24 percent polymer (Table III). The amount of polymer taken up by the skins was again estimated by nitrogen determination. Visual examination of the treated but unfinished skins

TABLE II

USE OF PERSULFATE/BISULFITE REDOX SYSTEM IN THE GRAFT POLYMERIZATION OF ETHYL ACRYLATE (EA) ON CHROME-TANNED NIGERIAN SHEEPSKINS

Expt. No.	Treatment Given*	Atmosphere	% Polymer in Product†	T_s (°C.)
1	1% $K_2S_2O_8$, 1% Surfactant	Air	0	98
2	1% Surfactant	N_2	0	97
3	1% $K_2S_2O_8$ 0.33% $NaHSO_3$	Air	4.6	99
4	1% $K_2S_2O_8$ 0.33% $NaHSO_3$ 1% Surfactant	Air	6.0	98
5	Same as Expt. 3	N_2	22.0	98
6	Same as Expt. 4	N_2	19.0	95

*Treatment on eight-inch squares using 200 percent water and 25 percent EA, in addition to the reagents listed. All percentages are based on the neutralized blue weight.

†Percent polymer calculated from nitrogen determinations. Value for control (no polymer), 17.43 percent.

revealed they had an increased thickness, appeared more uniform, and felt much as though they had been fatliquored. These skins, along with an untreated chrome-tanned sheepskin as a control, were converted into finished garment leather at a tannery. The resulting leather was then tested for tensile strength, ball burst strength, and stitch tear strength. The results are given in Table III.

The thickness measurements in all test specimens confirmed the opinions based on the visual examination of the unfinished stock, that the skins containing polymer were thicker. In almost all cases, the breaking load which had to be applied to the specimen was lower for the control than for the treated samples. The exception was obtained with the leather containing 24 percent poly(ethyl acrylate) (Expt. 2) for the tensile strength and the stitch tear strength. This skin did not compare well at all for some unknown reason. It may have been the skin or the polymer. With the lesser amount of poly(ethyl acrylate) (13 percent, Expt. 3) an improved product was actually obtained. However, the volatility and lachrymatory effects of this monomer preclude its use in tanneries. For comparison with the butyl acrylate product (Expt. 3), it should be pointed out that polymerization with ethyl acrylate actually caused decreases in the elongation in the tensile strength test and in the extension in the ball burst test.

The leather containing poly(butyl acrylate) appeared to be the best product for several reasons. The leather was in most cases the thickest and was fairly uniform over the entire skin. It withstood the greatest breaking load in all cases

TABLE III

EFFECT OF GRAFT POLYMERIZED ACRYLATE ESTERS ON THE STRENGTH PROPERTIES OF SHEEPSKIN GARMENT LEATHER

			Tensile Strength				Ball Burst				Stitch Tear		
Expt. No.	Treatment Given*	% Polymer in Product†	Thick. (in.)	Elong. (%)	Load (lbs./	Tensile (lbs./ in.^{2})	Thick. (in.)	Ext. (in.)	Load (lbs.)	Burst Strength (lbs./ in.)	Thick. (in.)	Load (lbs.)	Tear Strength (lbs./ in.)
1	10% EA	13	0.032	59	78	4910	0.040	.385	124	3100	0.046	37	900
2	25% EA	24	0.030	57	62	4120	0.045	.390	96	2135	0.041	15	365
3	25% BA	13	0.039	76	90	4600	0.047	.680	144	3065	0.043	40	930
4	None	0	0.026	64	65	5090	0.033	.400	91	2760	0.030	16	535

*Treatment on full chrome-tanned Nigerian sheepskins using 200 percent water, one percent potassium persulfate, 0.33 percent sodium bisulfite, one percent surfactant, and a carbon dioxide atmosphere. All percentages are based on the neutralized blue weight. EA is ethyl acrylate and BA is butyl acrylate.

†Calculated from nitrogen analyses.

TABLE IV

EFFECT OF GRAFT POLYMERIZED BUTYL ACRYLATE ON THE STRENGTH PROPERTIES OF KANGAROO ATHLETIC SHOE LEATHER

			Tensile Strength				Ball Burst				Stitch Tear		
Expt. No.	Treatment Given*	% Polymer in Product†	Thick. (in.)	Elong. (%)	Load (lbs.)	Tensile (lbs./in.²)	Thick. (in.)	Ext. (in.)	Load (lbs.)	Burst Strength (lbs./in.)	Thick (in.)	Load (lbs.)	Tear Strength (lbs./in.)
1	10% BA	5	.036	49	113	6215	.035	.320	108	3085	.038	30	790
2	25% BA	10	.041	54	151	7265	.043	.375	170	3955	.038	66	1740
3	None	0	.033	51	118	7110	.037	.400	138	3730	.035	35	1000

*Treatment on full chrome-tanned kangaroo skins using 200 percent water, one percent potassium persulfate, 0.33 percent sodium bisulfite, one percent surfactant, and a carbon dioxide atmosphere. All percentages are based on the neutralized blue weight. BA is butyl acrylate.

†Calculated from nitrogen analyses.

and had the greatest elongation and extension. This leather also had a high degree of area stability. It returned to its original shape and dimensions after being stretched repeatedly.

We realize that these tests were performed on separate skins and that, for completely valid comparisons to be made, matched side experiments should (and will) be run. However, in defense of these results, the chrome-tanned skins used were selected for uniformity. In addition, for the treatment which showed the greatest promise, the treatment with butyl acrylate, the improvements observed are considerable, averaging around 40 percent for the loads needed to break, burst, or tear the leather.

Also, the water vapor permeability of these leathers was measured. Analyses of the results indicated that there were no differences between the products containing the polymer and the controls. The fact that this was not adversely affected by the graft polymerization may be considered an asset.

The same treatment was applied to chrome-tanned kangaroo skins using two levels of butyl acrylate (Table IV) and, along with an untreated chrome-tanned skin for a control, these were finished into athletic shoe leather at a tannery. The leather was submitted to the same tests as the sheepskin garment leather and the results are given in Table IV. The leather with the greater amount of poly(butyl acrylate) (Expt. 2) showed higher strength properties than the control (Expt. 3), while that with the lesser amount (Expt. 1) appeared to be somewhat lower in strength. In this latter case however, the differences were minimal. As was the case with sheepskin, the water vapor permeability of the leather was not adversely affected.

For a number of reasons, the graft polymerization treatment with butyl acrylate shows great promise. The treatment appears to accomplish some of the objectives of post-tanning operations now used widely in leather making, such as fatliquoring, impregnation, etc. The product thus obtained had a greater uniformity and thickness and a higher degree of area stability, and was stronger than comparable products not containing the polymer. Also, this polymer is, at least partially, covalently bonded to the protein of the leather. These properties would all indicate an application in the manufacture of garment leather. Other applications will become obvious as more is known of the process and the properties of these products.

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DISCUSSION

DR. DONALD F. HOLLOWAY (Rohm and Haas Company): Certainly the incorporation of acrylic polymers in the leather is a subject of wide interest. We know in our experience anyway that one of the most often asked questions we have is about the incorporation of polymers into leather, especially since the introduction of aqueous table impregnation, which Mr. Korn touched upon lightly. Subsequently there was a great deal of work done on drum impregnation using acrylic polymers. This seems to be a field of great interest. We have seen a technique demonstrated to us here that opens a new door or a new approach to drum impregnation, although it is early in the investigation. Now I would like to ask for questions from the floor. I would think there would be much interest in this particular subject and I can state that we found the paper to be of extreme interest. Are there any questions?

Dr. William C. Prentiss (Rohm and Haas Company): On a couple of your slides, Mr. Korn, you noted that there was not a complete takeup of the monomer charged by the tanned hide substance or stock. Then you mentioned a little later that, in the case of 2-ethylhexyl acrylate, some of the monomer appeared to be on the surface, giving this sticky, tacky feel. But by and large what happens to the monomer that doesn't become incorporated?

Mr. Korn: We noticed that when the experiment is completed most of the 2-ethylhexyl acrylate monomer is found in the spent liquor. In fact, the spent liquor separates into two components on standing. Most of the monomer remains in the non-aqueous phase and is not grafted onto the substrate.

Dr. Prentiss: Another facet about polymerization — you are using a pseudo-emulsion technique and adding redox initiator systems. Normally you develop a fair amount of heat. What temperatures did you reach in these cycles, or were you able to get a measurement of it?

A. H. Korn: No, we haven't gotten around to measuring temperature increases in the course of running our graft polymerization experiments.

Dr. Prentiss: Do you have a qualitative way of estimating? Does it get real hot?

Mr. Korn: To the best of my knowledge the temperatures of the graft polymerization solutions don't increase much above room temperature.

Dr. Prentiss: Not too much over room temperature?

Mr. Korn: Not at least to our knowledge; isn't that right, Steve?

Dr. S. H. Feairheller (Eastern Regional Research Laboratory, U.S.D.A.): These reactions proceed at a slow enough rate that there is very little or no heat generated.

Dr. Prentiss: They are slow. Well, that would indicate that there is a time factor in processing, and approximately what time scale would be involved in completing a reaction?

Mr. Korn: We run our experiments for 24 hours. I think that is probably far too long but we haven't made any time studies yet to see what the optimum period would be. It might be just a few hours, but we run them for 24 hours as a matter of course.

Dr. Prentiss: Those were the questions I had in mind; thank you very much, Mr. Korn.

Dr. Holloway: Is there a question over there?

S. M. De (Garden State Tanning Company): I was wondering whether you tried anything like gamma radiation for getting a site in the protein chain for incorporation of this polymer?

MR. KORN: We have no facilities at our laboratory for doing radiation work. However, at the Southern Laboratory they are doing studies of this type, and we may eventually go into a coöperative study with them on irradiation initiation. But that is something for the future and that is something that I don't think very many tanners would be able to implement in their tanneries.

MR. DE: I was mentioning these things because I think gamma radiation will not affect that as much as a ceric persulfate initiation system. Irradiation would not affect the protein chain so much, so that we can have more leather character and at the same time we can have this polymeric incorporation.

MR. KORN: That is true. Ceric salts and persulfates are very powerful oxidizers and they undoubtedly do some damage to the leather and disrupt the collagen molecule.

DR. ROSS G. DONOVAN (Canada Packers, Ltd.): Two questions, if I may. First of all, it wasn't clear to me what your conclusions were as to the point of attachment of the polymer.

MR. KORN: We believe that the polymer is permanently attached to the hide protein. That is, it is actually chemically bonded, not loosely combined.

DR. DONOVAN: To which amino acid or to what residue does it appear to be bound?

MR. KORN: The complete mechanism is not very well understood but we think the polymer probably forms a carbon-carbon linkage with some of the segments of the collagen backbone that have been disrupted by the persulfate or the ceric ion.

DR. DONOVAN: I thought perhaps there was an implication in the abstract that it was attached to tyrosine.

MR. KORN: Our amino acid analyses indicate that tyrosine and other hydroxyamino acids do act as sites of polymer attachment. However, since these amino acids form only a minor portion of the composition of collagen, they could not account for all the polymer uptake. Therefore, we believe that there must be additional sites of polymer attachment.

DR. DONOVAN: Anwar (Proceedings Canadian Federation of Biological Societies, 1971, **14**, 118 (#455)) has recently shown that permanganate-periodate will destroy tyrosine in elastin. I think that such an oxidation is a possible explanation for your lost tyrosine. I noticed on one of your slides that you had what appeared to be a significant increase in serine, and I wondered if you have a possible answer for that.

MR. KORN: That is probably an artifact. We do get some variations of that type occasionally with our amino acid analyses. If they are too pronounced we